Porphyrinylboranes Synthesized via Porphyrinyllithiums.

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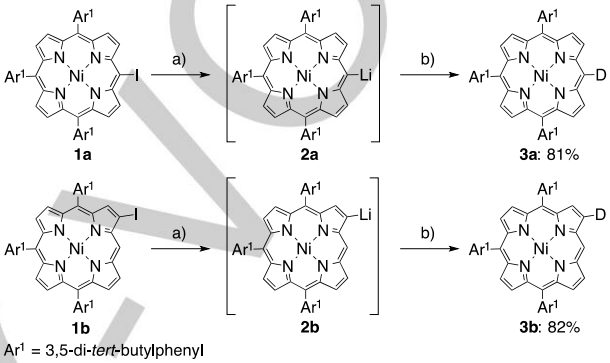
Keisuke Fujimoto,[a] Hideki Yorimitsu,*[a,b] and Atsuhiro Osuka*[a]

Abstract: As the most nucleophilic porphyrins, *meso*- or *β*-lithiated porphyrins were generated by iodine-lithium exchange reactions of the corresponding iodoporphyrins with *n*-butyllithium at –98 °C. Porphyrinyllithiums thus prepared were used for synthesis of dimesitylporphyrinylboranes via reactions with fluorodimesitylborane. The boryl groups proved to serve as an electron-accepting unit to alter the photophysical and electrochemical properties. In addition, 5-diarylamino-15-dimesitylboryl-substituted donor-accepter porphyrins showed increased intramolecular charge-transfer character in the S_1 state. Furthermore, the reaction of *β*-lithiated porphyrin with dichloromesitylborane provided a boron-bridged porphyrin dimer, which exhibited a conjugative interaction between two porphyrin units through the vacant p-orbital on the boron center.

In recent years, triarylboranes have attracted considerable attention in light of their intriguing features such as high luminescence properties, large nonlinear optical responses, and anion-sensing properties.[1,2] Owing to the high electrophilicity of three coordinate borons, bulky aryl substituents have been often employed to protect the boron center from nucleophilic attack. Considering the rich optical and electrochemical properties of porphyrins, porphyrinylboranes that can be regarded as a hybrid of porphyrin and triarylborane would be interesting functional molecules. The first peripheral borylation of porphyrins has been accomplished by Therien and co-workers.[3] The resulted bononates were proved to be useful building blocks for Suzuki-Miyaura cross-coupling. However, installation of a diarylboryl group directly on the periphery of porphyrins has remained unexplored so far. Reactions of nucleophilic porphyrinyl reagents with haloboranes would be a feasible synthetic route to porphyrinylboranes. However, generation of such porphyrin reagents has not been easy because porphyrin cores are reactive toward nucleophilic species to undergo various transformations.[4]

Recently, we succeeded in preparation of porphyrinyl Grignard reagents as a rare example of nucleophilic porphyrin species through iodine-magnesium exchange under cryogenic conditions.[5,6] These Grignard reagents displayed high nucleophilicity toward aldehydes and ketones. Inspired by the success, we embarked on the synthesis of porphyrinylboranes by using porphyrinyl Grignard reagents. As an initial attempt, we examined the reaction of a porphyrinyl Grignard reagent generated from *β*-iodoporphyrin **1b**[7] (Ar^1 = 3,5-di-*tert*-butylphenyl throughout the manuscript) with fluorodimesitylborane (Mes_2BF). A bulky dimesitylboryl group was employed to protect the boron center in the product from moisture and oxygen. However, the reaction was sluggish and gave the desired borylated product **4bNi** only in 17% yield. *meso*-Magnesioporphyrin prepared from *meso*-iodoporphyrin **1a**[8] was entirely unreactive toward Mes_2BF and only decomposition of the Grignard reagent was observed. These disappointing results should stem from the insufficient nucleophilicity of these porphyrinyl Grignard reagents.



Scheme 1. Preparations of porphyrinyllithiums **2a** and **2b**. a) *n*BuLi (1.5 equiv), THF, –98 ºC; b) D_2O (excess).

We then envisioned the preparation of porphyrinyllithiums as more reactive porphyrinyl nucleophiles via iodine-lithium exchange (Scheme 1). After iodine-lithium exchange between **1a** and *n*-butyllithium[9] at –80 ºC, an addition of D_2O afforded *meso*-deuterioporphyrin **3a**[6] (57%) along with protodeiodinated product (12%) and *meso*-butylated product (7%). These results indicated not only the formation of *meso*-lithiated porphyrin **2a** but also the occurrence of undesirable side reactions. Indeed, Senge and co-workers reported that nucleophilic addition of organolithium reagents to porphyrin cores was extremely fast and occurred even at –100 ºC in THF.[4b] However, after extensive optimization, we found that the iodine-lithium exchange of **1a** with *n*-butyllithium proceeded preferentially over the nucleophilic addition to **1a** in THF at –98 ºC to give **3a** in 81% yield. Generation of *β*-lithiated porphyrin **2b** has been similarly confirmed by the formation of *β*-deuterated product **3b**[6] from **1b** in 82% yield under the same conditions.

To our delight, we have found that porphyrinyllithiums **2a** and **2b** are reactive enough toward fluorodimesitylborane to give **4aNi** and **4bNi** in 52% and 70% yields, respectively (Scheme 2). Importantly, these dimesitylporphyrinylboranes are tolerable under basic and acidic conditions owing to the sterically protected boron center. Thanks to their high stability, **4aNi** and **4bNi** underwent reductive denickelation with 4-tolylmagnesium bromide[10] followed by zincation to yield **4aZn** and **4bZn**, respectively. The solid-state structures of **4aNi** and **4bNi** have been revealed by X-ray crystallographic analysis (Figure 1). The boron center on *meso*-borylporphyrin **4aNi** shows a propeller-like structure with C—B bonds of 1.57–1.58 Å, which are typical lengths for sterically crowded triarylboranes.[11] The boron atom is embedded in a completely planar geometry with the sum of ∠C—B—C angles to be 360º. The dihedral angle between the

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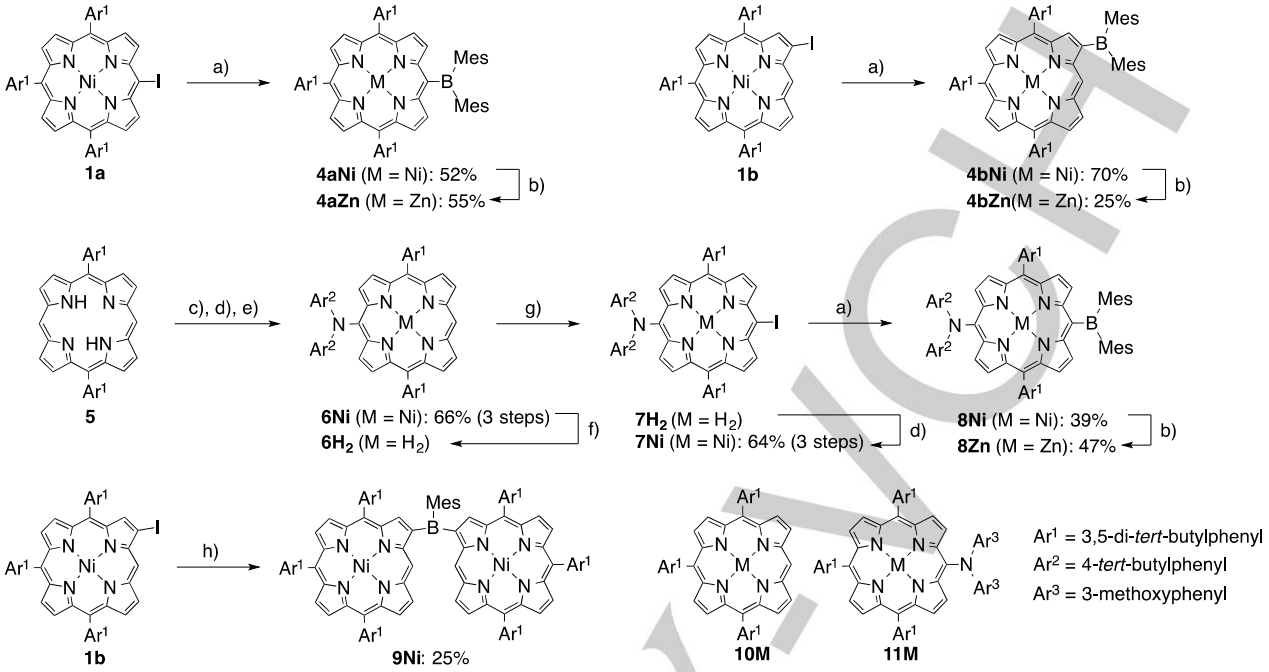

Scheme 2. Synthesis of porphyrinylboranes **4aM**, **4bM**, **8M**, and **9Ni** and structures of reference compounds **10M** and **11M**. a) *n*BuLi (1.5 equiv), THF, –98 ºC, then fluorodimesitylborane (1.5 equiv), r.t.; b) 4-TolMgBr (10 equiv), toluene, 60 ºC (for **4aNi** and **8Ni**) or 40 ºC (for **4bNi**), then $Zn(OAc)_2$, CH_2Cl_2/MeOH, r.t.; c) NBS (1.0 equiv), pyridine, $CHCl_3$, 0 ºC; d) $Ni(acac)_2$, toluene, reflux; e) di(4-*tert*-butylphenyl)amine (3 equiv), Pd-PEPPSI-IPr (10 mol%), NaO*t*Bu (3 equiv), THF, reflux; f) conc. H_2SO_4/TFA, 0 ºC; g) I_2 (1.5 equiv), PIFA (1.5 equiv), pyridine, $CHCl_3$, 0 ºC; h) *n*BuLi (1.1 equiv), THF, –98 ºC, then dichloromesitylborane (0.55 equiv), r.t..

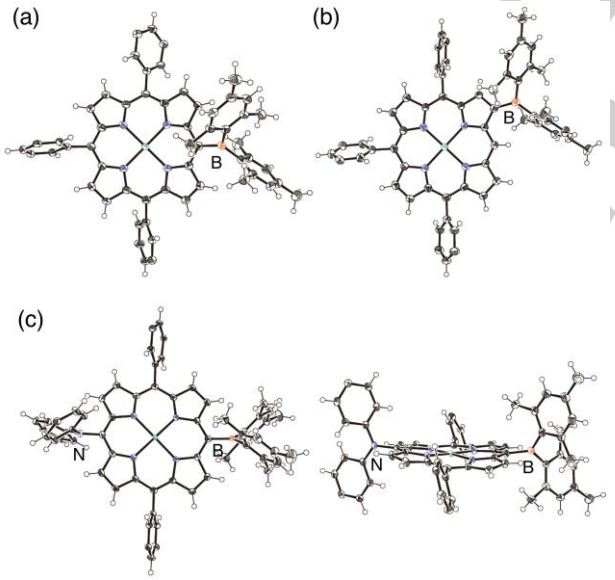

Figure 1. X-ray crystal structures of (a) **4aNi**, (b) **4bNi**, and (c) **8Ni**. The thermal ellipsoids are scaled to 50% probability. Solvent molecules and *tert*-butyl groups are omitted for clarity.

dimesitylboryl plane and the porphyrinic plane is 43º, suggesting a moderate stereoelectronic interaction between the boron atom and the porphyrin π-plane. In contrast, the structure of *β*-boryl **4bNi** shows a smaller dihedral angle between the boron unit and the porphyrinic plane (25.2º) and a shorter C—B bond (1.552 Å), which suggest a more effective p-π* interaction between the *β*-boryl group and porphyrin network owing to the sterically less hinderednature of *β* position.

In the next step, we attempted to synthesize a donor-acceptor type porphyrin bearing a diarylamino group and a diarylboryl group on the porphyrin periphery. *meso*-Amination of **5** was accomplished via *meso*-bromination with *N*-bromosuccinimide followed by Pd-catalyzed Buchwald-Hartwig amination under Pd-PEPPSI-IPr/NaO*t*Bu conditions.[12] Di(4-*tert*-butylphenyl)amine was employed as a coupling partner to avoid competitive halogenation on the diarylamino segment in the next reaction. The free *meso*-position of **6Ni** was iodinated with iodine/bis(trifluoroacetoxy)iodobenzene (PIFA)[8] via more electron-rich free-base porphyrin **6H₂** to furnish **7Ni** in 64% yield. **7Ni** was subjected to the same iodine-lithium exchange conditions followed by treatment with Mes_2BF to give **8Ni** in 39% yield. Ni^{II} porphyrin **8Ni** was further converted to the corresponding Zn^{II} porphyrin **8Zn** via denickelation with 4-tolylmagnesium bromide and subsequent zincation in 47% yield. The structure of **8Ni** has been revealed by X-ray crystallographic analysis to possess planar geometries both at the boron and nitrogen atoms, as indicated by the sums of ∠C—B—C and

∠C—N—C angles of 360º and 359º, respectively. These planar segments are tilted toward the porphyrin plane with dihedral angles of 57º and 77º, respectively.

Absorption and fluorescence spectra were taken to investigate the electronic properties of porphyrinylboranes (Figure 2). The absorption spectrum of *meso*-borylated **4aZn** showed a sharp and intense Soret band at 432 nm and weak Q bands at 558 and 601 nm. Both bands were red-shifted by *ca*. 20 nm compared to those of the corresponding triaryl Zn^{II}-porphyrin (**10Zn**). *β*-borylated **4bZn** exhibited almost the same absorption spectrum as that of **4aZn**. **4aZn** and **4bZn** exhibited slightly enhanced fluorescence representing mirror images of their Q bands. The absorption spectrum of 5-diarylamino-15-dimesitylboryl porphyrin **8Zn** exhibited a characteristically broad Soret band similar to *meso*-diarylaminoporphyrin (**11Zn**)[13] with a bathochromic shift in its Q band by 20 nm. Porphyrin **8Zn** shows relatively large Stokes shifts that depend on solvent polarity; 623 cm^{-1} in hexane, 828 cm^{-1} in toluene, 883 cm^{-1} in $CHCl_3$, 1079 cm^{-1} in CH_2Cl_2, and 1164 cm^{-1} in nitromethane (see Figures S31, 32 in SI). These data suggest increased charge transfer character in the S_1 state. The charge transfer character of **8Zn** was also supported by theoretical calculation (see Figures S34 in SI). While the orbital coefficients are almost localized on the porphyrin unit in the frontier orbitals, **8Zn** shows delocalised orbitals over the diarylamino and dimesitylboryl moieties in the HOMO and LUMO, respectively.

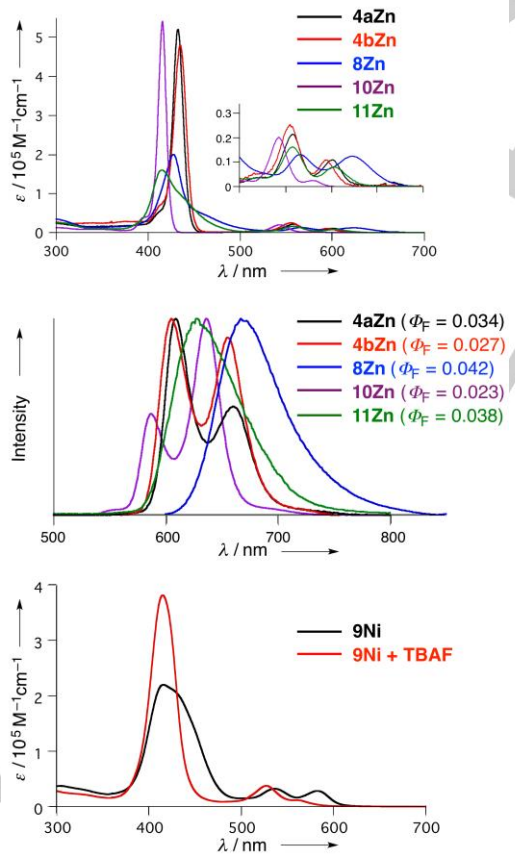

Figure 2. (a) UV/Vis absorption and (b) fluorescence spectra of **4aZn**, **4bZn**, **8Zn**, **10Zn,** and **11Zn** in CH_2Cl_2. (c) UV/Vis spectra of **9Ni** in CH_2Cl_2 and in CH_2Cl_2 with 1×10^{-4} M TBAF.

Upon addition of tetrabutylammonium fluoride (TBAF), the absorption of **4aNi** and **4bNi** were blue-shifted (see Figure S33 in SI) by disruption of the p-π* interaction by B-F coordination. In order to make this coordination effect clearer, we designed a boron-bridged porphyrin dimer **9Ni**, which is supposed to show π-conjugation between two porphyrin units through the vacant p-orbital on the boron atom. Thanks to the high reactivity of *β*-lithiated porphyrin **2b**, two-fold nucleophilic substitution of dichloromesitylborane[14] successfully provided **9Ni** in 25% yield.[15] **9Ni** were quickly purified by silica-gel column chromatography because **9Ni** gradually decomposed under ambient conditions. The instability toward moisture or oxygen implies insufficient kinetic stabilization at the boron center. High-resolution atmospheric-pressure-chemical-ionization time-of-flight (HR-APCI-TOF) mass spectrum of **9Ni** exhibited the ion peak at *m*/*z* = 2024.0659 of $[M+Cl]^-$ (calcd. for $C_{133}H_{153}N_8{}^{11}B^{35}Cl^{58}Ni_2$; 2024.0731). The ^1H NMR spectrum of **9Ni** showed two singlets and six doublets in the range of 9.82–8.54 ppm due to the *meso*- and *β*-protons and three singlets at 7.11, 2.53, and 2.49 ppm due to the protons of the mesityl group. The dimer **9Ni** exhibited a rather broad Soret band over 390–470 nm and red-shifted Q bands, owing to the conjugative electronic interaction between two porphyrins via the vacant p-orbital of the boron atom. Upon addition of TBAF, the Soret band became sharpened[16] as a consequence of the disruption of the conjugative interaction between two porphyrins.

Electrochemical properties were revealed by cyclic voltammetry (Table 1). The parent unsubstituted Zn^{II} triarylporphyrin **10Zn** shows first oxidation potential of 0.36 V, and first reduction potential of –1.86 V. The reduction potentials of **4aZn** and **4bZn** were positively shifted by *ca*. 0.1 V. **8Zn** also shows a positively shifted reduction wave compared to **11Zn**. Thus, their electrochemical HOMO–LUMO gaps (ΔE_{HL}) decreased by *ca*. 0.1 eV owing to their enhanced electron-accepting characters.

Table 1. Redox potentials of **4aZn**, **4bZn**, **8Zn**, **10Zn**, and **11Zn**.

Compound	$E_{ox.2}$ (V)	$E_{ox.1}$ (V)	$E_{red.1}$ (V)	ΔE_{HL} (eV)
4aZn	0.64	0.35	–1.78	2.13
4bZn	0.67	0.36	–1.77	2.13
10Zn	0.66	0.36	–1.86	2.22
8Zn	0.46	0.23	–1.77	2.00
11Zn	0.48	0.27	–1.83	2.10

[a] The redox potentials were measured by cyclic voltammetry in anhydrous CH_2Cl_2 with 0.1 M Bu_4NPF_6 as supporting electrolyte and $Ag/AgClO_4$ as reference electrode. Fc/Fc^+ was used as external reference.

In summary, porphyrinyllithiums were successfully generated by iodine-lithium exchange reactions of the corresponding iodoporphyrins with *n*-butyllithium at –98 °C. The porphyrinyllithiums were useful for synthesis of a series of porphyrinylboranes via reactions with suitable haloboranes. The boryl groups proved to serve as an electron-accepting unit to alter photophysical and electrochemical properties. B,N-substituted donor-accepter porphyrin showed increased intramolecular charge-transfer character in the S_1 state and boron-bridged porphyrin dimer exhibited a conjugative interaction between the two porphyrin units through the vacant p-orbital at the boron atom. Further applications of porphyrinyllithiums and investigations on boron-containing porphyrinoids are currently underway.

Acknowledgements

This work was supported by Grants-in-Aid from MEXT (Nos.: 25107002 “Science of Atomic Layers”) and from JSPS (Nos.: 25220802 (Scientific Research (S)), 24685007 (Young Scientists (A)), 26620081 (Exploratory Research)). H.Y. acknowledges Kansai Research Foundation for Technology Promotion and The Asahi Glass Foundation for financial support. K.F. acknowledges a JSPS Fellowship for Young Scientists.

Keywords: porphyrin • halogen-lithium exchange • borylation • triarylborane • donor-acceptor porphyrin

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[15] Probably because of its highly crowded nature, a *meso*-to-*meso* boron-bridged dimer was not formed under the same reaction conditions using *meso*-lithiated porphyrin **2a**.

[16] Upon addition of TBAF, the full width at half maximun (fwhm) of the Soret band of **9Ni** was decreased from 3320 cm^{-1} to 1860 cm^{-1}. The Soret band of **9Ni-F⁻** is still larger than that (fwhm = 1190 cm^{-1}) of **10Ni** due to the exciton coupling interaction.

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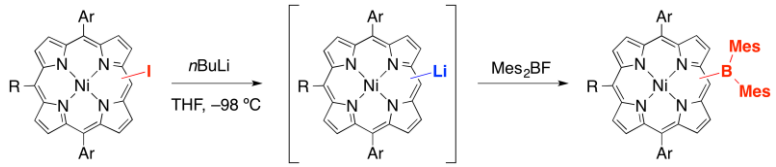

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